INROAD TO MODIFICATION AND FUNCTIONALIZATION OF THE DETONATION NANODIAMOND

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Abstract

Introduction. Diamond with its excellent mechanical, physical and chemical characteristics is now available from natural deposits or it can be produced both at thermodynamically stable and metastable synthesis conditions. Now widely developed detonation synthesis of nanodiamond(ND) [1-3] attracts still extended attention due to several remarkable reasons. First of all ND is one of modern nanomaterials, available from several suppliers in NIS, China, Japan and S.Korea, etc. in commercial scale achieving ton per year. Other privilege is that ND is genuine diamond, not converted to graphite phase at 1 atm and in vacuum and inert environment until 1000 ^{0}C and more. Thirdly ND have nearly spherical shape of individual particles not in wide range of dimensions 2 to 10 nm with average size close to 4.2 nm.

From the another side it reasonable to point out that actually ND is industrial semi-product due to: (1) non-diamond carbon impurities or non-carbon impurities (Fe, Cr, Ni, Al, Si, Ca, etc.) giving an ND sample a grey or dark grey appearance; (2) light elements mostly at the chemically bonded ND termination (oxygen ~ 10 wt. %, hydrogen ~1 wt. %) and nitrogen (~2 to 3 wt. %), mostly in the bulk; (3) the presence at ND surface chemical groups of C-H, C-OH, C-O-C, C=O, C=(O)H (aldehide), C=O (OH) (acid), C-NH_2, lactonic and other groups making the ND surface chemically multifunctional; (4) “ash-related” impurities (Fe, Cr, Al, Ca, Si etc.) with the total up to several wt. % occurring as free elements, oxides or carbides, both on the ND particle surface and in the bulk; (5) intrinsic impurities and those with zero- and higher dimensionality defects in the particle’s bulk, producing an appreciable excess of enthalpy (up to 25 kcal/kg); (6) one or more twin boundaries in the fractions of ND particles [6]; (7) a fairly strong agglomeration (agglutination) of individual particles which form tightly packed structures of tens, hundred or thousands of nanometers in size. Some of these characteristics do not permit considering ND as an individual nano-substance according to V.B.Aleskovsky’s definition.

Above listed reasons challenged us to efforts towards to modification and mono-functionalization of the ND.

Experimental. We have used ND sample supplied by New Technology Co. (Chelyabinsk, Russia). Before supplying the samples was finally cleaned by ozone.

Our approach include chemical interaction of the ND with hydrogen- (molecular hydrogen and ammonia) and chlorine-contained environment (carbon tetrachloride) at 1 atm and temperature in range 450 to 1100 ^{0}C.

It was established by Raman- and FTIR-spectroscopy some improvement of crystalline structure of the ND.

After 5 h interaction with hydrogen at 850 ^{0}C the heat of combustion of the ND is 1000 cal/g less relative initial ND. It suggest us about some annealing of defects after

Elaboration of the nanopowder at above condition.

FTIR-spectroscopy indicate appearance C-H, N-H and C-N groups after interaction with ammonia at 800^{0}C. Chemical analysis reveal up to 7 mass. % content of bonded chlorine after heating 1 h in CCl_4/Ar mixture at 450^{0}C. In the same time water absorbance became 10 times less in comparison wit initial powder.

Intensity of C-Cl band at 709 cm^{-1} in reflectance FTIR-spectra progressively rose with the interaction time.

Remarkable is rather modest diminishing – no more that 50 % of dangling bond content measured by ESR-spectroscopy after any of above treatment.

Finely it seems for us that there were find approach to control th behavior of community of the ND particles and systems like ND – solid substrate through intentional changing of the ND functionalization, e.g. hydrophilic/hydrophobic and/or acidic/basic. It might open more room for ND application in academic research and industrial practice.

We have suggested a simple and effective technique for vapor ND cleaning and functionalization. High temperature ND treatment allows the chemical agents to penetrate in nanoporous materials and functionalize the ND surface in a desired way. Hydrophilic/ hydrophobic or acid/base ND termination becomes feasible. We believe that this technique has a large potential in research and development projects[4]..

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